

Organotin compounds in technology and industry

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Professor Davies started working on organic peroxides in 1950, then put the peroxy group onto silicon in 1955. Over the years, this work was extended to the peroxides of other metals, including the first peroxytin compounds in 1962. That required an understanding of basic organotin chemistry, which at that time was fairly fragmentary, and led to a lifetime's interest in the subject. He has published many research papers and reviews in the field, and is the author of two editions of *Organotin Chemistry* and the co-editor of a further recent volume, *Tin Chemistry: Fundamentals, Frontiers, and Applications*.

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Organotin compounds find a bigger range of technological and industrial applications than the organic compounds of any other metal. Many of these applications involve catalysis or anticatalysis, often in polymer chemistry, and they have an importance out of all proportion to the tonnage of tin which is used. This article reviews the present standing of the non-biological applications of organostannanes, with an emphasis on the mechanisms of the reactions which are involved.

Keywords: organotin compounds, catalysis, industrial technology

1. Introduction

The three major families of organometallic compounds which find application in technology and industry are those based on aluminium, silicon, and tin.

Alkylaluminium compounds are highly reactive, and their applications depend on their chemical properties as alkylating agents, for example, towards tin tetrachloride in the production of alkyltin compounds.

Organosilicon compounds, on the other hand, find applications which depend more on their physical properties. Carbon–silicon and silicon–oxygen bonds are strong and the polysiloxanes (silicones) are kinetically and thermally stable, resistant to oxidation, hydrolysis, and heat, and are strongly hydrophobic. They find use, for example, as oils, rubbers, resins, sealants, and mould release agents.

Organotin compounds show a more even balance of reactivity and stability. Unlike the organoaluminium compounds, they are usually stable enough to be handled in air, but when they carry suitable functional groups they can take part in a wide variety of reactions, and they are used in the laboratory as reagents for organic synthesis. They are also versatile in their applications in industry and technology, and this is the subject of the present review.

Monoorganotin compounds, RSnX_3 , find rather few applications. As catalysts, the diorganotin compounds are usually preferred, but the mono- and di-organo compounds are used in conjunction in PVC stabilisation, and butyltin trichloride is finding increasing use in the vapour phase deposition of an SnO_2 film on glass.

The diorganotin compounds, R_2SnX_2 , have a low mammalian toxicity, and are used principally as stabilisers for poly(vinyl chloride), as catalysts for the formation of polyurethanes and polysiloxanes and for a variety of reactions at carboxyl centres, and for the chemical vapour deposition of films of SnO_2 .

The triorganotin compounds are much more biologically active and have been used in agriculture and wood treatment as pesticides and fungicides, though these uses have diminished in recent years because of concerns about their broader toxicity in the environment.^{1,2} A major use has been in the treatment of hulls of ships to prevent fouling by weeds. This is banned now because of the effect it was having on shellfish and molluscs in bays and coastal waters, but a brief account is included here (Section 8) because of its technological interest and current developments in which the technology is being extended to other metals.

Apart from their use in glass coating (Section 7), the principal current applications of organotin compounds thus are in catalysis or anticatalysis (Sections 3–6), particularly in the plastics industry. The tonnage of the metal which goes into organotin compounds is therefore small compared with that which goes into tin plating or solder, but the benefits which accrue from it are out of all proportion to the amount of tin which is involved.

The previous reviews of the field do not cover developments in the past decade, and most emphasise commercial aspects rather than the chemistry which underlies the applications and which is highlighted here.^{3–6} Two books^{3,4} from the International Tin Research Institute in 1985 give particularly good early surveys of the field.

2. Industrial preparation of organotin compounds⁷

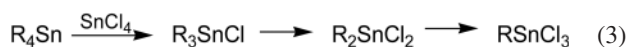
On the industrial scale, organotin compounds are usually prepared by alkylation of SnCl_4 with organo-magnesium or -aluminium compounds.

Grignard reagents, RMgX , are prepared from the metal and an alkyl or aryl halide and need large volumes of solvent and are expensive. It is difficult to restrict their reaction with SnCl_4 to partial alkylation unless R is very bulky, and the reaction

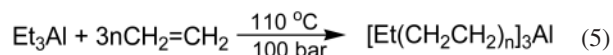
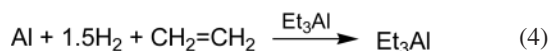
is usually taken to completion to give R_4Sn [equations (1) and (2)].



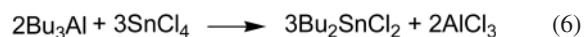
The tetraalkylstannane is then heated with the appropriate amount of $SnCl_4$ (the Kocheshkov reaction) when redistribution occurs to give the alkyltin chlorides R_nSnCl_{4-n} [equation (3)].



Triethylaluminium can be made from aluminium metal, hydrogen and ethylene [equation (4)], and higher alkylaluminium compounds are then made by the Ziegler growth reaction between triethylaluminium and ethylene, which needs no solvent [equation (5)]. Trimethylaluminium, which is strongly dimerised, does not give this reaction, so it is the even-numbered alkylaluminium compounds, *e.g.* $n-Bu_3Al$ and $(n-C_8H_{17})_3Al$ which are readily accessible.



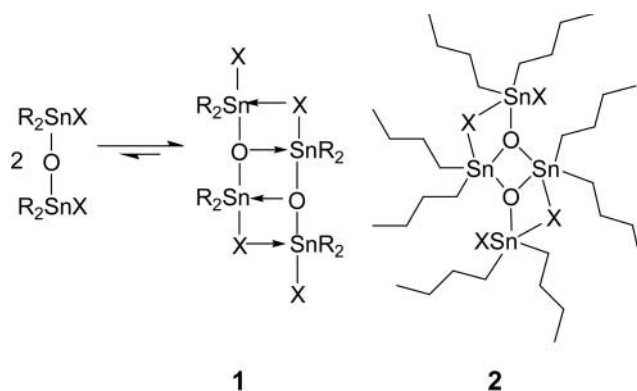
These organoaluminium compounds react with $SnCl_4$ to give the corresponding alkyltin chlorides, and unlike the Grignard reagents, these reactions can be taken to the stage of partial alkylation to give the alkyltin halides directly, *e.g.* equation (6). Dibutyl- and dioctyl-tin dichloride are made industrially by this method.



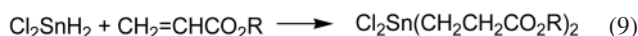
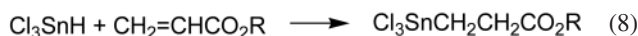
Other organotin derivatives can then be made from these chlorides. For example, treatment with sodium acetate gives the corresponding organotin acetates, and thiols under basic conditions give the tin thiolates, both of which are used as stabilisers for PVC. Progressive hydrolysis of dibutyltin dichloride gives first the dichlorodistannoxane which is used extensively as a catalyst, and then dibutyltin oxide which is an insoluble polymer [equation (7)].



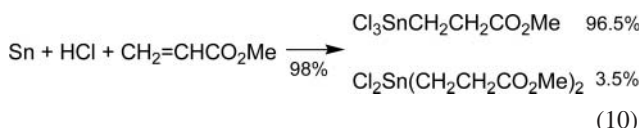
These difunctional distannoxanes, $XR_2SnOSnR_2X$, are ladder-shaped dimers (1) which are highly soluble in non-polar solvents because they have the structure of a reversed micelle (2), with a polar core surrounded by lipophilic alkyl groups,⁸ and they are excellent catalysts for a number of organic reactions apparently because of their nature as binary Lewis acids.



An alternative method of forming the SnC bond was introduced in 1976 by the AKZO company [equations (8) and (9)]. HCl Gas reacts with metallic tin or with $SnCl_2$ in an ethereal solvent to give the solvated hydrochlorides $HSnCl_3$ and H_2SnCl_2 . These add heterolytically to acrylic esters to give β -alkoxycarbonyl ethyltin compounds [equations (8) and (9)].⁹⁻¹¹



The two reactions can be combined, as shown in equation (10).



Substitution of the chlorine by thioalkyl groups then gives a family of PVC stabilisers (the "estertins") as described below.

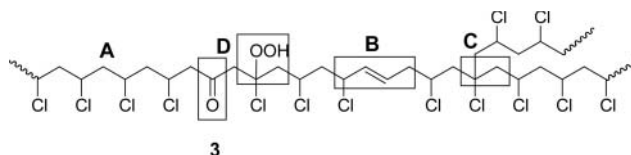
Extensive efforts have been made to prepare organotin compounds by the direct reaction of metallic tin with organic halides, but the only process which as yet has been commercially successful is the preparation of dimethyltin dichloride from methyl chloride and tin in the presence of a catalyst [equation (11)].



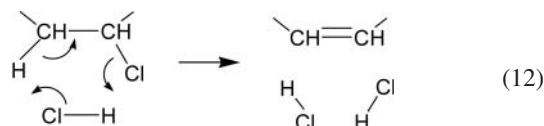
3. Stabilisation of PVC¹²

Poly(vinyl chloride) (PVC) is the third most widely used plastic, after polyethylene and polypropylene, with an annual consumption of about 30 million tonnes, into which go about 75,000 tonnes of organotin stabiliser.¹² The unplasticised (rigid) polymer is used in supply pipes and domestic drainage and in the construction industry in, for example, window profiles and cladding. Plasticised PVC is used in various forms of packaging such as "blister packs", blow-moulded bottles and food wrapping.

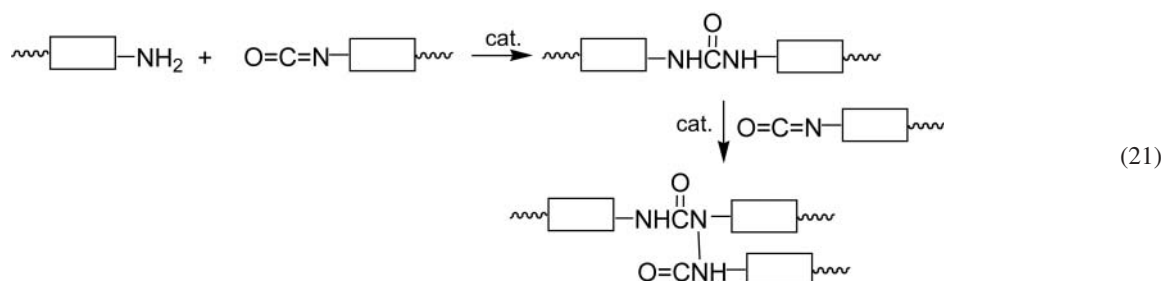
The polymer is prepared by the polymerisation of vinyl chloride, $(CH_2=CHCl)$, in suspension, emulsion, bulk, or solution, by a radical mechanism. The regularity of the $(CH_2CHCl)_n$ chain (A) is interrupted by defect sites of unsaturated groups (B), branches (C), and oxidised structures (D), as illustrated in formula 3.¹³



The unplasticised polymer has a high melting point, and in making PVC sheet, the polymer is calendered between rollers heated to about 200 °C. Pipes and other profiles are made by extrusion, and bottles by blow moulding. Under these conditions, HCl is eliminated starting from the defect sites, particularly the unsaturated positions which typically are present to the extent of about 1 per 1,000 monomer units. The liberated HCl catalyses further elimination, perhaps by the mechanism shown in equation (12).

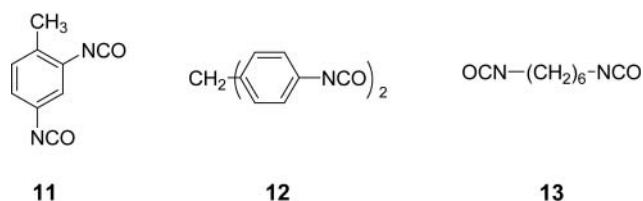


This progresses along the chain in a zipper fashion, to give an extended conjugated polyene [equation (13)] which absorbs

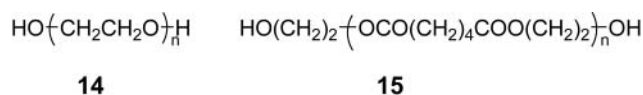


Cross-links are introduced by the incorporation of some triol such as glycerol. If water is present, hydrolysis of the isocyanate generates carbon dioxide [equation (20)] which blows the polymer into a foam. The amine which is also formed then goes on to give a urea link in the polymer chain and further reaction of the isocyanate at the urea moiety may give a biuret cross-link [equation (21)]; alternatively, a blowing agent such as CO_2 , a hydrocarbon, or a fluorohydrocarbon may be passed into the polymerising mixture to create the foam.

Typical isocyanates which are used are toluene 2,4-diisocyanate (**11**), bis(4-isocyanatophenyl)methane (**12**), and hexamethylene diisocyanate (**13**).



The diols may typically be based on polyethylene oxide (**14**) or polypropylene oxide, or a diester-diol co-oligomer, *e.g.* **15**.



An alternative approach is to use a “screened” isocyanate in which a reagent HX has been added to the isocyanate [equation (22)]; typical screening agents are phenols, oximes, caprolactam and 3,4-dimethylpyrazole. In the polymerisation process, HX is replaced by the diol. These screened isocyanates are used particularly in coatings. This process has been thoroughly reviewed by Wicks.²²

By either method, organotin compounds are used to catalyse the formation of the polyurethane; dibutyltin dilaurate is very commonly used. Table 1 shows the relative rates of the model reaction of phenyl isocyanate with methanol in the presence of some organotin catalysts.

In injection moulding, the diol and diisocyanate, containing the catalyst and other components, are injected into the mould and cured. The rate of cure determines the turn-round rate of the process.

The manufacture of a foam involves sophisticated technology. The diisocyanate, diol, and catalyst are mixed, together with any necessary filler, cross-linking polyol, antioxidant, blowing agent, or surfactant (to stabilise the foam) and the

Table 1 Relative rates of reaction of phenyl isocyanate and methanol in the presence of organotin catalysts

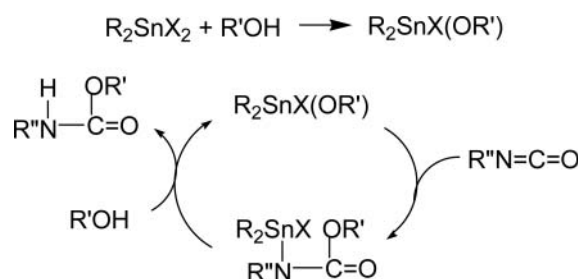
Catalyst	Relative rate
None	1
Bu_2SnCl_2	200
$\text{Bu}_2\text{Sn}(\text{OCOMe})_2$	30,000
$(\text{Bu}_2\text{SnO})_n$	40,000
$\text{Bu}_2\text{Sn}(\text{OCOC}_{10}\text{H}_{21})_2$	56,000

foam is extruded from the reactor as a continuous block; obviously, the balance between the rates of blowing the foam and the setting of the foam is crucial and governs the choice of the catalyst.

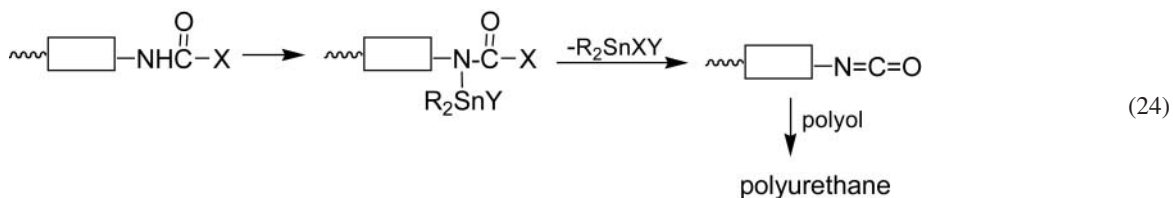
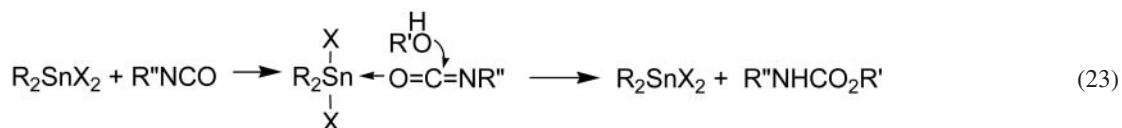
Organic coatings, sealants, and adhesives usually involve aliphatic isocyanates. A one-component formulation might consist of an isocyanate-terminated prepolymer (low polymer) and catalyst in a solvent such as toluene. On exposure to air the solvent evaporates to leave a film and curing is brought about by moisture which joins the chains through urea linkages as in equations (20) and (21). A heat-cured paint may use a blocked urethane.

Two basic mechanisms have been proposed for the formation of the urethane linkage from the isocyanate and alcohol, involving either a direct insertion of the isocyanate into an Sn–O bond, or the organotin derivative acting as a Lewis acid.

In the former mechanism, the catalyst R_2SnX_2 reacts with the alcohol $\text{R}'\text{OH}$ to give the tin alkoxide $\text{R}_2\text{SnX}(\text{OR}')$ or $\text{R}_2\text{Sn}(\text{OR}')_2$. The isocyanate then rapidly inserts into the Sn–O bond to give an *N*-stannylcarbamate, which rapidly react with the alcohol to give the urethane and regenerate the catalyst (Scheme 1). These individual steps can be confirmed in isolation; the insertion step is reversible.^{23,24}



Scheme 1 Insertion of an isocyanate into a tin alkoxide.

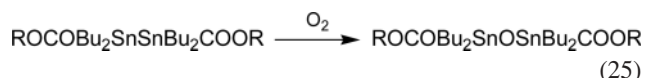


The mechanisms by which the tin compound operates as a Lewis acid are suggested to be important with the tin chlorides or carboxylates which do not readily exchange their ligands with the alcohol. Three variants have been proposed. In the first two, the organotin catalyst in the above cycle is 5-coordinated as either $R_2SnX_2(HOR')$ or $R_2SnX_2(OR')^-$. Third, association of the isocyanate with R_2SnX_2 may enhance its reactivity towards nucleophilic attack by the alcohol [equation (23)].

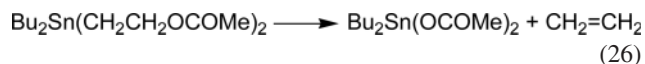
The masked isocyanates have been proposed to react with the glycols by either an elimination-addition or addition-elimination sequence, catalysed by organotin compounds. Amides readily undergo stannylation at nitrogen, and the addition of the Sn-X bond to isocyanates is often reversible, particularly at the higher temperatures which are used for curing the paint on car bodies, and the organotin catalyst may well promote the elimination-addition route [equation (24)].

Jousseume has shown that the difunctional tetrabutyl-distannoxanes, $XR_2SnOSnR_2X$, are effective catalysts, and they may operate as binary Lewis acids, as described below.²⁵

Masked organotin catalyses have also been devised to permit the use of a one-component mixture which is stable until it is exposed to air or heat. The tetrabutyl-diacyloxydistannanes are inert until they are air-oxidised to the distannoxanes when they become efficient catalysts [equation (25)].²⁶

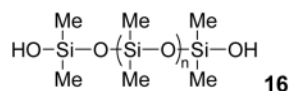


Similarly the 2-carboxyethyltin compounds are non catalytic, but at elevated temperatures, ethene is eliminated to give the catalytic tin carboxylates [equation (26)].



5. Room temperature vulcanisation of silicone polymers

The third group of polymers in which the organosilicon compounds are involved are the silicones, particularly poly(dimethylsiloxane) (16) and its copolymers.



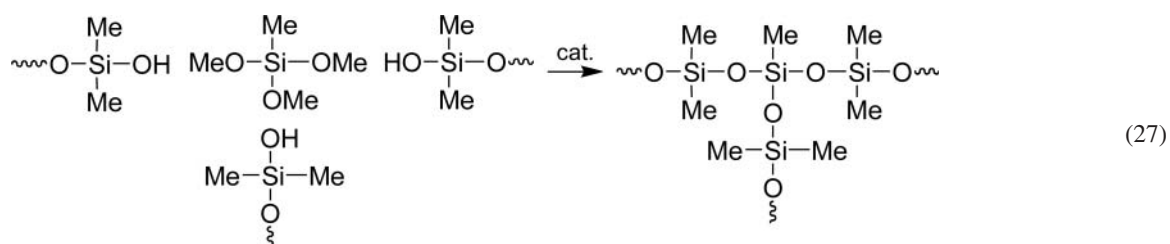
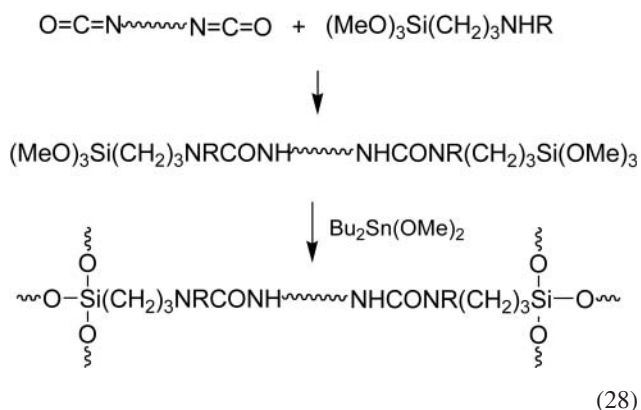
Cross-linking of the chains converts the silicone oils into elastomers with a wide variety of uses such as coatings, sealants, moulding compounds, release agents, encapsulants, and water repellents.

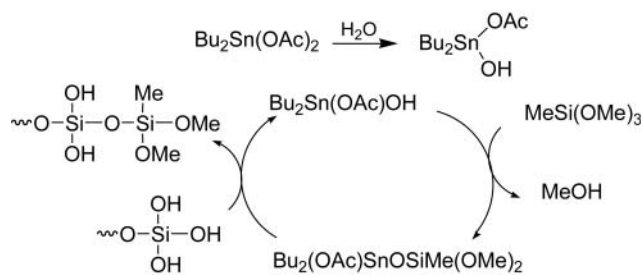
This vulcanisation can be carried out at room temperature (room temperature vulcanisation, RTV) with a tri- or tetra-functional silane as a cross-linking agent and an organotin catalyst, which is commonly dibutyltin diacetate or dilaurate [equation (27)].

The product may be supplied in two components, one consisting of the HO-terminal polysiloxane and the other containing the tri- or tetra-methoxysilane and the organotin catalyst, and reaction occurs when the components are mixed.

A one-component product would contain a mixture of a MeO-terminal polysiloxane, the polyfunctional cross-linker, and the catalyst. When the mixture is exposed to air, the terminal MeO groups are hydrolysed to OH, and vulcanisation takes place.

A silanol-terminated silicone co-polymer can be cross-linked in the same way, and isocyanate-terminated polyurethanes can be end-capped with trialkoxysilyl groups and then subjected to vulcanisation, *e.g.* equation (28).²⁷





Scheme 2 Mechanism of RTV of a silicone.

Silylethyl groups can be grafted onto polyethylene by treating it with the vinylsilane $(\text{RO})_3\text{SiCH}=\text{CH}_2$ in the presence of a free radical initiator, and then these grafts can be cross-linked by hydrolysis which is catalysed by an organotin compound.

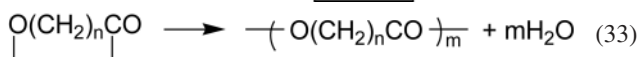
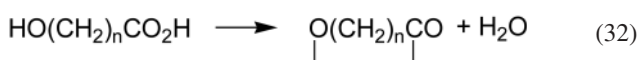
Little work has been done on the mechanism of the cross-linking, but the picture put forward by van der Weij in 1980 is generally accepted (Scheme 2).²⁸

The organotin dicarboxylate is first hydrolysed to the hydroxyl carboxylate. This reacts with the trialkoxysilane cross-linker to give a stannasiloxane, and this in turn reacts with terminal hydroxylsilane groups of the polymer to cap it with a dimethoxysilane group. Repetition of this process gives a cross-linked polymer.

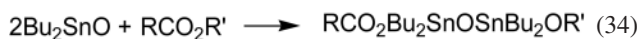
Jousseume's latent distannane catalyst can also be used for curing silicones.²⁶

6. Transesterification and related reactions

Reactions at carboxyl groups, such as esterification, transesterification, transcarbamoylation, lactonisation, and ring-opening polymerisation (ROP) [equations (29–33)], are important in chemical industry.

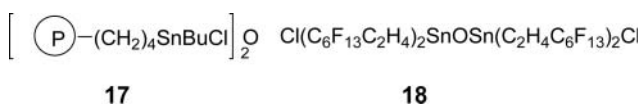


These reactions can generally be catalysed by alkalis or protic acids, but frequently a less aggressive catalyst is needed because the reactants may be acid- or base-sensitive, or for avoiding corrosion of the plant, or for environmental reasons, and organotin compounds are commonly used for this purpose. This is currently a very active field of study. Dibutyltin dilaurate and dibutyltin oxide are frequently used; the latter compound is an intractable polymer, but it dissolves on reaction with the carboxyl compound to give a distannoxane, *e.g.* equation (34).



The dichlorodistannoxane, $\text{ClBu}_2\text{SnOSnBu}_2\text{Cl}$, [see equation (7)], and other difunctional distannoxanes are particularly effective, and are widely used.^{29,30} When they are used for catalysing the esterification between a carboxylic acid and an alcohol, however, the distannoxanes are immediately decomposed to give the dialkyltin diacetates, and any catalysis is by the protic acid HX which is thereby formed.³¹

Tetraphenyltin has been shown to be effective for some reactions (*e.g.* the dehydropolycondensation of *L*-lactic acid³²), but the actual catalyst is probably a triphenyltin compound, Ph_3SnX , which is formed by dephenylation. To avoid problems in recovering the organotin catalysts, polymer-supported catalysts (*e.g.* **17**)³³ and fluoros distannoxane catalysts (*e.g.* **18**)^{34,35} have been developed.³⁶

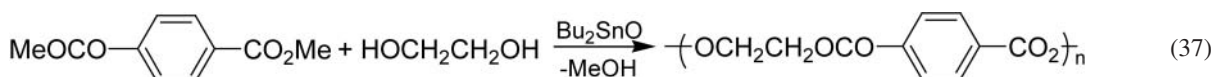
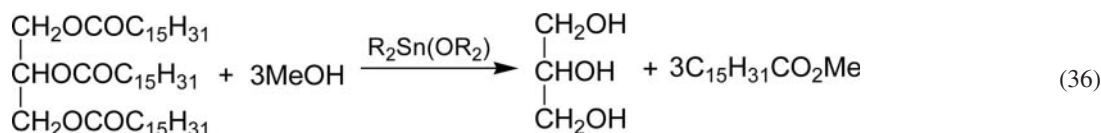
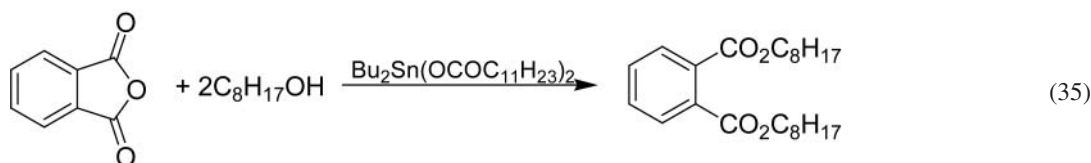


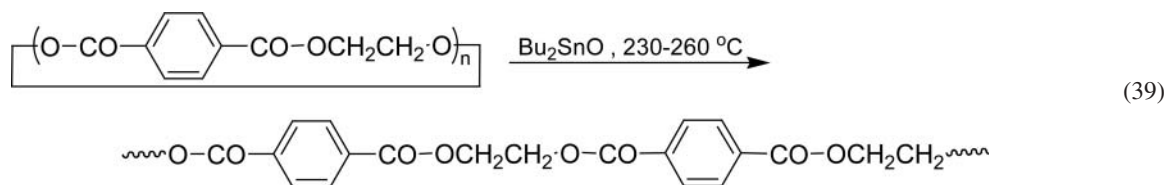
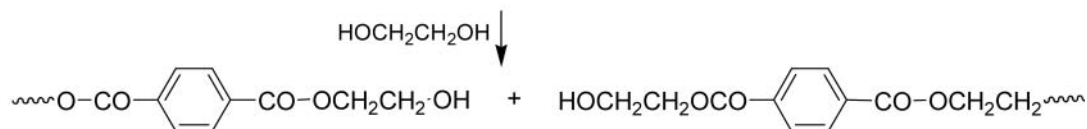
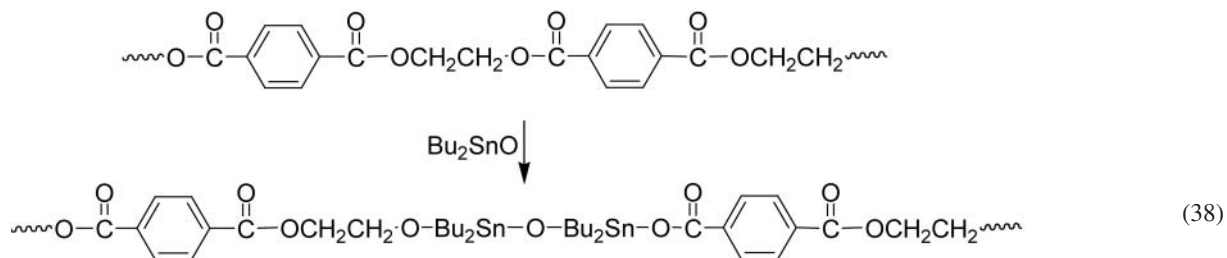
Thus dialkyl phthalates, which are used as plasticizers, can be made from phthalic anhydride and an alcohol with dibutyltin dilaurate as catalyst [equation (35)].

A simple example of transesterification is given by the reaction of methanol with palmitin, which is the main constituent of palm oil, to give methyl palmitate, which can be used in place of diesel oil in internal combustion engines [equation (36)].³⁷

Poly(ethylene terephthalate) (PET), which is used in fibres (Terylene, Dacron), or for packaging, or for blow-moulded bottles (Mylar, Melinex), can be produced by transesterification of dimethyl terephthalate with ethylene glycol [equation (37)].^{38,39}

For recycling the polymer, poly(ethylene terephthalate) (*ca* 200-mer) can be transesterified with an excess of various diols⁴⁰ at 180–270 °C over several hours in the presence of

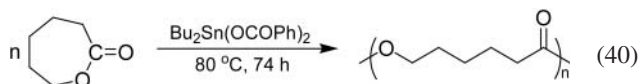




Bu_2SnO to give an oligomer (ca 8–10-mer) [e.g. equation (38)], which can be used for recycling the polymer, or for reacting with an isocyanate for preparing a polyurethane.⁴¹ The reaction can also be carried out without solvent in a twin-screw extruder with a residence time of 1 min.⁴⁰

The waste PET polymer can also be converted into ethylene terephthalate cyclic oligomers which undergo ring-opening polymerisation (ROP) with dibutyltin oxide to regenerate the polymer [equation (39)].⁴²

Most polymers which are used in the medical field for implants, sutures, or drug-release are resorbable aliphatic polyesters formed by the ring-opening polymerisation of lactones such as ϵ -caprolactone. This is catalysed with aluminium alkoxides or organotin alkoxides, chlorides or carboxylates, or 1,3-difunctional tetraalkyldistannoxanes [equation (40)].⁴³

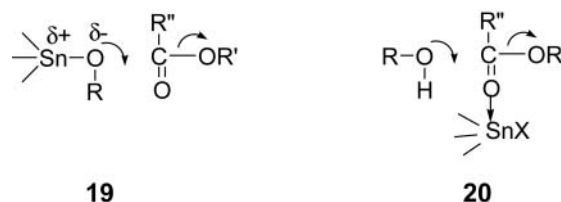


Block copolymers of hydroxytelechelic poly(ethylene terephthalate) from reaction in equation (38), and carboxytelechelic poly(ϵ -caprolactone), can be prepared with the residual organotin catalyst which is used in the glycolysis of PET [equation (38)].⁴¹

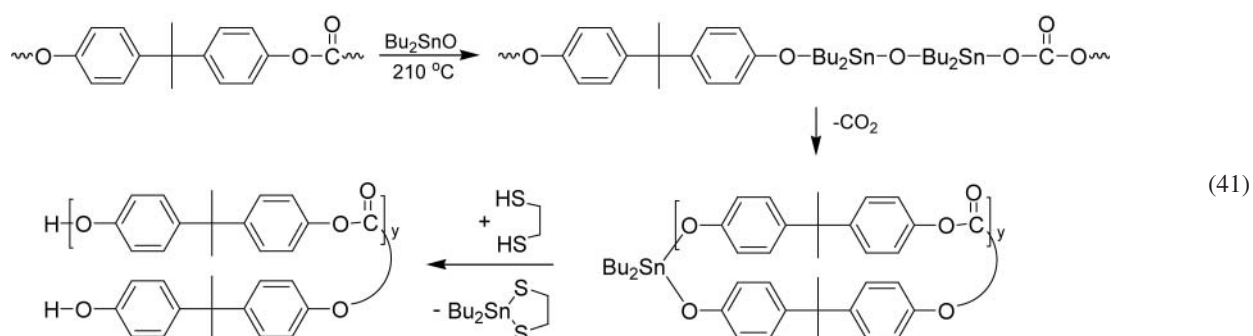
Controlled degradation of polycarbonates, which are used in CDs and DVDs, to oligocarbonates can be brought about with dibutyltin oxide. For example, poly(bisphenol-A carbonate)

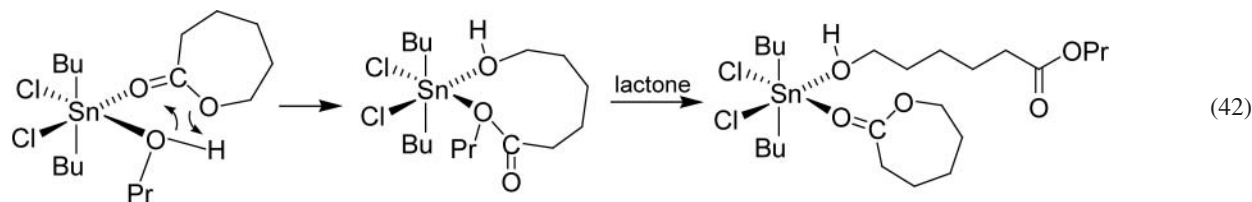
reacts with Bu_2SnO in a 10:1 molar ratio, with evolution of CO_2 , to give what are probably Bu_2Sn -containing cyclic oligocarbonates rather than linear polymers. The tin can then be removed with ethylene dithiol to give a hydroxytelechelic oligo(bisphenol-A carbonate) of one-tenth of the size of the starting polymer, and this can then be further modified [equation (41)].⁴⁴

A similar dichotomy of mechanism as in the addition to isocyanates applies to the mechanism of these substitution reactions at carboxyl groups. The organotin catalyst may react with the alcohol to give an alkoxide, enhancing the nucleophilicity of the alkoxy group (19), or it may react as a Lewis acid towards the carboxyl group, increasing its electrophilicity (20).



The former mechanism probably applies when the catalyst is introduced as the organotin alkoxide, or oxide, or carboxylate,⁴⁵ and Otera showed that in the reaction between ethanol and ethyl acetate in toluene at 100 °C the dimethoxide and the diacetate were converted into $\text{AcOBu}_2\text{SnOSnBu}_2\text{OEt}$,



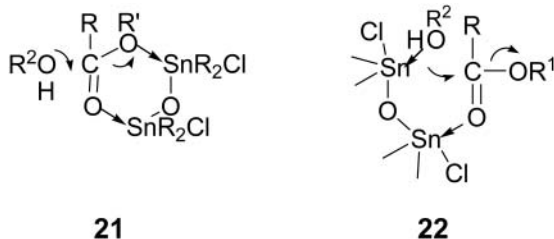


supporting this picture. The organotin chlorides, however, which do not readily undergo alcoholysis, appear to survive the reaction unchanged, and to behave as Lewis acids.

Thus for the polymerisation of ϵ -caprolactone by dibutyltin dichloride initiated by propanol, it was concluded that both the lactone and the alcohol coordinated to the tin, then ring-opening was brought about by nucleophilic attack of the alcohol at the acyl group of the neighbouring lactone ligand [equation (42)].⁴⁶

The situation is similar with the distannoxane catalysts. Jousseume showed that $\text{ClBu}_2\text{SnOSnBu}_2\text{Cl}$ was recovered unchanged from the (symmetrical) transesterification of ethyl acetate with ethanol,⁴⁷ and from the transcarbamoylation of *N*-hexyl *O*-methyl carbamate with octanol [equation (43)].²⁵

In both reactions, the catalyst appears to operate as a pure Lewis acid, and its efficiency derives from its nature as a double Lewis acid which can hold the two reagents in juxtaposition. Both the acyl and the alkyl oxygen atoms of the carboxylate might coordinate to the distannoxane (21), or only the acyl oxygen, with the alcohol held at the second tin centre near to the acyl carbon centre at which it reacts (22).



Dimethyl carbonate is an environmentally benign chemical with an increasing number of uses, but it is commonly prepared from phosgene, and an alternative route from carbon dioxide would obviously be better. A direct synthesis has been

developed from methanol and supercritical CO_2 with dibutyltin dimethoxide as the catalyst. The water which is eliminated deactivates the catalyst, but, at 200 atm and 180 °C, if the water is removed by circulating the reactants through a molecular sieve,⁴⁸ a yield of the carbonate of about 46% can be obtained.

The water presumably hydrolyses the dimethyltin dimethoxide to the distannoxane $\text{MeOBu}_2\text{SnOSnBu}_2\text{OMe}$, and a mechanism which is in accord with the evidence is shown in Scheme 3.

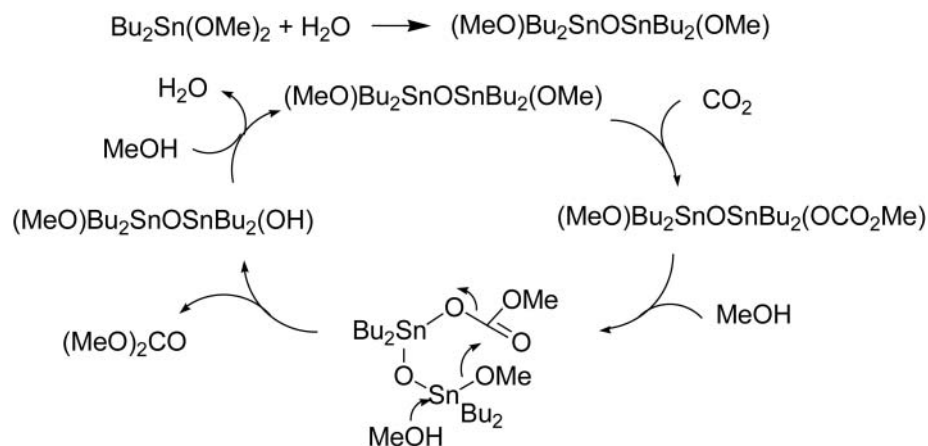
This is probably an oversimplification. The distannoxane will be present mainly as a dimer (though possibly in equilibrium with the monomer under the reaction conditions), and a decanuclear stannoxane, which may be represented as two parallel five-rung ladders, each consisting of two $(\text{Bu}_2\text{Sn})_2\text{O}$ units with Bu_2SnOMe units at each end, with these ladders end-bridged by two carbonate groups.⁴⁹

7. Coating glass with tin oxide

Thin films of SnO_2 deposited on various solid substrates have a variety of important applications.^{50,51,52} A layer, 1- μm thick, fills in imperfections in the surface and strengthens the glass so that thinner bottles can be used (e.g. milk bottles) which use less glass and are subject to fewer breakages.

If the SnO_2 is doped with about 3% of fluoride it becomes an *n*-type semiconductor; the band gap between the filled and empty orbitals is reduced into the infrared region, making the glass transparent to solar radiation, but reflective toward heat radiation. This principle is used in designing low-emissivity window glazing (Pilkington's K glass ®), as illustrated in Fig. 1.

Doping with antimony and with indium is also common, though the latter (ITO, indium tin oxide) has a largely indium content. These semiconductors are used in a variety of electronic devices such as diodes, transistors, solar cells, heated windows, antistatic coatings, and sensors.



Scheme 3 Formation of dimethyl carbonate from methanol and CO_2 .

In 1974, ablative self-polishing paints were introduced, and their mode of action is illustrated in Fig. 2. They contained a copolymer of, typically, methyl methacrylate and tributylstannyl methacrylate (Fig. 2A), designed to leach tributyltin at a constant rate of $1.6 \mu\text{g cm}^{-2}$ per day. The resulting acrylic acid (Fig. 2B) copolymer is hydrophilic and is ablated off by the motion of the ship, exposing a fresh tin acrylate surface (Fig. 2C), and a steady release of Bu_3SnX can be achieved. When the ship is stationary in harbour, the rate of leaching is much less. The paint provided protection for 5 to 7 years, and the hull did not need cleaning before repainting. In 1987, the amount of tributyltin compounds used in antifouling paints in 1987 was reported to be about 450 tons.

However, the tributyltin which was released into the water turned out to be toxic to shellfish and molluscs such as oysters. The use of these paints was progressively restricted in the 1980s and a ban on their use came into effect in January 2008, but the technology that was developed is now being adapted to the design of self-polishing copper polyacrylates which work on the same principle.

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